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ELECTROCHEMICAL PROPERTIES OF METAL COMPLEXES OF DITHIO-ACID DERIVATIVES AND THEIR APPLICATION IN EXTRACTION POLAROGRAPHY

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Summary—Metal complexes with dithiocarbamic (dtc), xanthic (xan) and dithiophosphoric (dtp) acids give rise to one or more polarographic waves in dimethylformamide and in mixtures of extracting solvents and ethanol. The electrons are found to be transferred stepwise in the case of unfilled *d*-shell metal complexes. The shift of half-wave potential depends on the ligand, increasing in the order dtp < xan < dtc. In solvents with low solvation power the electrode processes are more reversible. The linear dependence of the limiting current on the chelate concentration has been used for determining the metal in the organic phase without re-extraction. Pb(II), Bi(III) and As(III) have been separated with dtp as extractant, and the concentrations of Co(II), Ni(II) and Zn(II) complexes (simultaneously extracted) have been determined polarographically.

Metal complexes formed with various substituted dithio-acids have recently found wide application in analytical chemistry. Dithio-acids and their simple salts are of great importance as reagents for extraction, separation and determination of metal ions by various methods, mainly photometric.[1–4] The use of dithio-acids in extraction polarography can be successfully applied for solving new analytical problems. The effective application of this method requires a systematic and detailed investigation of the electrochemical behaviour of the metal complexes in non-aqueous media.

This paper presents data on the electrochemical reduction of some metal complexes formed with the dithio-compounds given in Table 1. Cyclic chronovoltamperometry and d.c. and a.c. polarography were employed. Dimethylformamide (DMF), acetonitrile (AN), and 2:3 v/v mixtures of benzene, toluene, *m*-xylene, chloroform, ethylacetate or isoamyl alcohol with methanol were used as solvents.

EXPERIMENTAL

Apparatus

The polarographic measurements were performed with an LP-7 polarograph (Czechoslovakia), PO-5122 oscillographic polarograph model 03 (USSR) and a.c. polarograph PPT-1 (USSR). All voltammetric measurements were made with a three-electrode cell at 25 ± 0.2°. The dropping mercury electrode (d.m.e.) was used as the working electrode for recording the current–voltage curves. At 25 cm mercury pressure and zero applied voltage, the characteristics of the capillaries used were: $m = 2.96$ and 0.61 mg/sec and $t = 4.81$ and 7.50 sec respectively. The experiments were carried out with a drop-time of 0.5 sec (electromechanical device). The auxiliary electrode was a mercury pool. The reference electrode consisted of a mercury pool in a DMF solution of tetraethylammonium perchlorate, placed in a glass tube ending in a cracked glass-bead junction with the bulk solution.

Reagents

The dithio-acids and their salts and metal chelates were synthesized by methods reported in the literature.[5–8] Their purity was checked by determining the m.p. and by elemental analysis. The organic solvents were purified by a standard technique. The supporting electrolytes used were 0.1*M* tetraethylammonium perchlorate in DMF and 0.2*M* lithium perchlorate in ethanol. All solutions of the complexes were prepared in solvent previously deoxygenated with purified hydrogen.

RESULTS AND DISCUSSION

The electrochemical behaviour of the complexes is best seen from the data obtained for DMF media. It is possible to identify two different systems of electrode reactions, corresponding to two types of process on the d.m.e.

All the complexes formed by metals with filled *d*-electron shells are reduced in DMF to the metal amalgams in one step. Electroreduction of the transition metal chelates formed by xan or dtp and the bivalent metal ions proceeds in a similar way. The diffusion-controlled current, i_d, is proportional to the concentration of chelate in the range $1–5 \times 10^{-4} M$, and practically independent of the mercury pressure head corrected for the back-pressure. Plots of $\log i_p$ *vs.* $\log V$ (i_p is the limiting current on the cyclic voltamperograms, V is the scan-rate of potential) exhibit slopes of 0.5. These results also suggest that the limiting currents are diffusion-controlled. Plots of $\log i/(i_d - i)$ *vs.* E are straight lines with a slope of approximately $60/n$ mV (n is the oxidation state of the central atom in the chelate) (Table 1). The limiting currents and microcoulometric analysis indicate that the waves for the Pb(II), Tl(I), Bi(III), Cu(II) and Hg(II) chelates correspond to the transfer of n electrons per molecule. From these results the wave appears to be reversible. This interpretation is supported by the parameters of